

Design and Evaluation of Ionic Liquids as Novel CO₂ Absorbents

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Abstract

Progress from the third quarter 2006 activity on the project “Design and Evaluation of Ionic Liquids as Novel CO₂ Absorbents” is provided. Major activities in two areas are reported: *property measurement* and *molecular modeling*.

We have measured CO₂ solubility in an ammonium lactate ionic liquid. Previous work has shown that the lactate anion enables chemical complexation to occur. We hypothesized that the lactate anion would not be as effective in complexing when paired with an ammonium cation as compared to when it is paired with an imidazolium cation. The results confirm this. We also measured CO₂ solubility in a functionalized ionic liquid containing an amine group. These so-called task specific ionic liquids (TSILs) are expected to have dramatically higher CO₂ solubility than physical absorbents. We report isotherms as well as entropies and enthalpies of absorption for CO₂ in one TSIL. CO₂ solubilities are higher in this compound than in any previous IL we have observed. Finally, we also developed a new simulation method that will enable us to compute full isotherms of gases in ionic liquids. So far, we have tested the method against model systems and found it to be highly effective.

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List of Graphical Materials

Figure 1: Isotherms for CO₂ in [N7777][lactate] at two temperatures.

Figure 2: Enhancement in solubility of CO₂ in [N7777][lactate] versus the benchmark[hmim][Tf₂N].

Figure 3: CO₂ isotherms for the TSIL [H₂NC₃H₆mim][Tf₂N]. This compound shows some of the highest CO₂ solubilities yet observed.

Figure 4: Proposed mechanism for CO₂ capture by a TSIL.

Introduction

Ionic liquids are a new and exciting class of compound that have the potential to overcome many of the problems associated with current CO₂-capture techniques. Ionic liquids (ILs) are organic salts that are liquid in their pure state near ambient conditions. ILs are regarded as potentially environmentally-benign solvents due to their immeasurably low vapor pressure, which essentially eliminates the opportunity for solvent release to the atmosphere.

The goal of this project is to obtain a fundamental understanding of the solubility of CO₂ and other components present in flue gas in ILs, with the practical objective of tailoring the properties of the liquid to maximize the engineering properties for this process. Our plan is to do this through a combination of *synthesis and experimental measurements*, *molecular simulation* and *applications development*. This ninth quarterly technical report (Q3 2006) describes the results of our work on this project from 07/01/2006 through 09/30/06).

Executive Summary

Ionic liquids (ILs) are organic salts that are liquid in their pure state near ambient conditions. They are a new and exciting class of compound that have the potential to overcome many of the problems associated with current CO₂-capture techniques. This project is concerned with developing a fundamental understanding of the solubility of flue gas species (mainly CO₂) in ionic liquids. Using this knowledge, we hope to develop new IL compounds that can be used in a cost effective manner for CO₂ capture. During Q2 2006, we have focused on two major activities: *synthesis of new ionic liquids*, and *CO₂ solubility measurement*.

Physical Property Measurement

We measured CO₂ isotherms in tetraheptylammonium lactate ([N777][lactate]) at 25 °C and 60 °C. We find that the solubility is lower than when an imidazolium cation is paired with lactate, thus confirming our hypothesis that the high CO₂ solubility previously observed with an imidazolium lactate ionic liquid lactate anion was the result of the extraction of a hydrogen from the C2 position of the imidazolium ring. We measured CO₂ solubility in an amine-bearing ionic liquid and found very high solubility, due to chemical complexation.

Molecular Simulations

We developed and tested a new simulation procedure called continuous fractional component Monte Carlo (CFC MC) for simulating gas absorption isotherms in liquids. This technique will be required to simulate gas solubility in ionic liquids. To date, we have only tested the method against model systems, but anticipate applying it to ionic liquids in the next quarter.

Experimental

Gas absorption was measured using a gravimetric microbalance, as described in our previous reports.

Results and Discussion

Property Measurement

CO₂ solubilities were then measured at 25°C and 60°C in [N7777][lactate]. Results are shown in Figure 1.

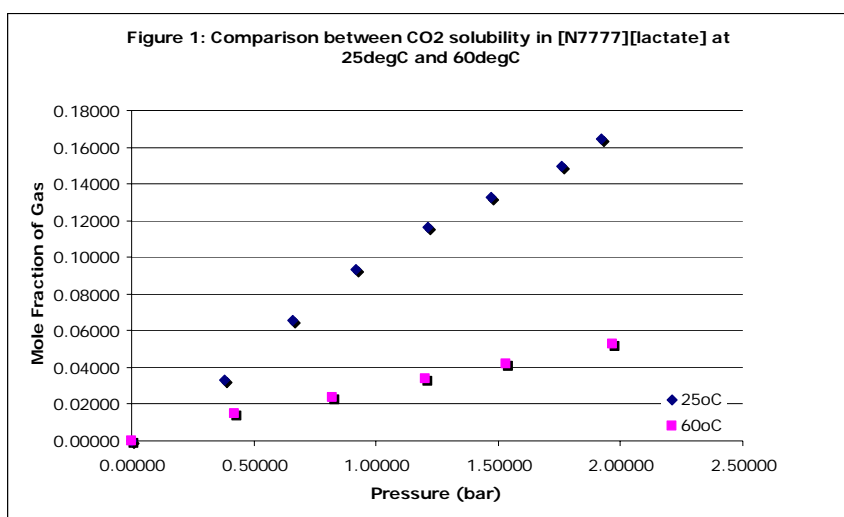


Figure 1: Isotherms for CO₂ in [N7777][lactate] at two temperatures.

When the CO₂ solubility is compared with that of a baseline IL such as [hmim][Tf₂N] at 25 °C (see Figure 2), you can see that the solubility of CO₂ is higher in the lactate IL. This is good news, since the lactate anion is much cheaper than the [Tf₂N]] anion. However, the solubility is still lower than the solubility of CO₂ in a known chemically complexing lactate-based IL such as the amine-containing ionic liquid shown in Figure 3. Thus, the [N7777][lactate] is better than most physical absorbents, but does not complex as greatly as some other compounds. We believe the reason is that, in the presence of a dialkylimidazolium cation, the lactate anion abstracts a proton from the C2 position of the

imidazolium ring, enabling the formation of a zwitterion. This mechanism is not operative with the ammonium cation, and so the CO₂ solubility is lower.

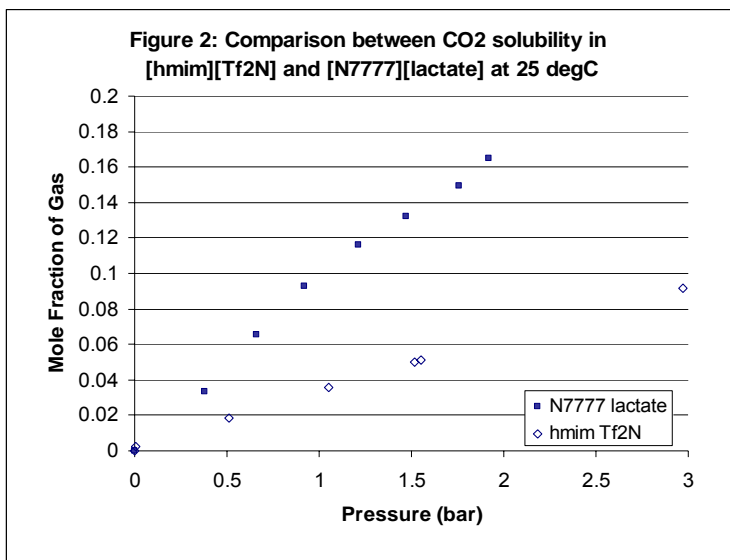


Figure 2: Enhancement in solubility of CO₂ in [N7777][lactate] versus the benchmark[hmim][Tf₂N].

We synthesized a task specific ionic liquid (TSIL) containing an amine functional group on the alkyl tail of a butyl chain attached to an imidazolium ring. This TSIL has the formula [H₂NC₃H₆mim][Tf₂N] and is the same compound originally made by Davis and co-workers¹. We then measured the CO₂ isotherms for this TSIL, with results shown in Figure 3. The results show that this TSIL has the highest CO₂ solubility we have observed. We hypothesize that the mechanism of CO₂ capture is similar to that of a conventional amine. That is, the CO₂ pairs with two amine groups to form a carbamate species, as shown in Figure 4. We will need to conduct NMR investigations to confirm this.

By measuring the temperature dependence of the Henry's constant, the partial molar enthalpy and entropy of absorption can be determined. Table 1 shows the results.

	Value	Error	Units
$\Delta h =$	-48.66	0.5	kJ/mol
$\Delta s =$	-154.8	1.5	J/mol K

Table 1: Partial molar enthalpy and entropy of CO_2 absorption in the TSIL.

We observe that the enthalpy of absorption is about 1/3 that of CO_2 in a conventional amine like MEA. Thus, we expect the regeneration heat duty to be less.

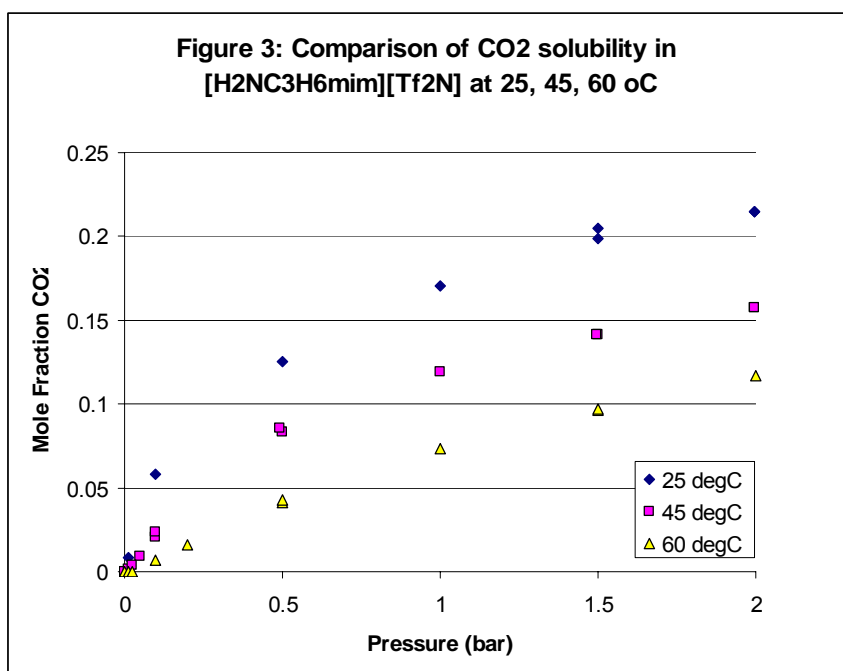


Figure 3: CO_2 isotherms for the TSIL $[\text{H}_2\text{NC}_3\text{H}_6\text{mim}][\text{Tf}_2\text{N}]$. This compound shows some of the highest CO_2 solubilities yet observed.

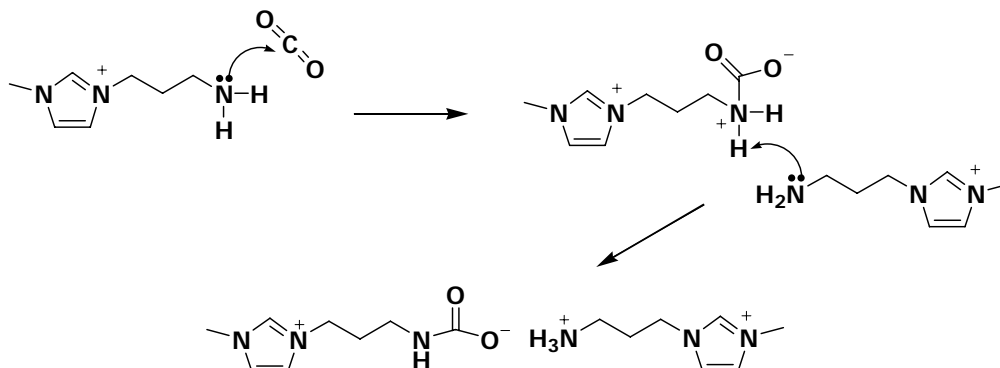


Figure 4: Proposed mechanism for CO_2 capture by a TSIL.

Simulations

Standard simulation methods for computing absorption isotherms in liquids fail when applied to ionic liquids, given their high density and strong electrostatic interactions. We have developed a new simulation method called continuous fractional component Monte Carlo (CFC MC) that we believe will enable us to compute isotherms for ionic liquids.

We have tested the method by carrying out simulations of the Lennard-Jones fluid and the simple point charge (SPC) model for water. We then compared the results against standard GCMC simulations and found that they agreed within the statistical accuracy of each simulation. Interestingly, without biasing, GCMC turned out to be very inefficient; even for the relatively simple system of pure water, only 0.007% of the insertions or deletions were accepted. In contrast, 1.2% of all transitions resulted in a change in composition for CFC MC. We are presently working to implement this new technique so that gas absorption in ionic liquids can be simulated.

Publications

A publication resulting from this work appeared: “Measurement of SO_2 solubility in ionic liquids” and is listed in the references².

Conclusions

We have measured isotherms for two new ionic liquids. Both show higher CO₂ solubility than the benchmark physical absorbent ionic liquid. The amine-functionalized ionic liquid shows great promise – it has the highest overall solubility and 1/3 the enthalpy of absorption as an amine solution. We have developed a new atomistic simulation technique for computing gas absorption isotherms and are in the final validation stages. We hope to apply it to CO₂ solubility in ionic liquids next quarter. Overall, we have completed all the project milestones to date, and are on track to meet the Q3 2006 milestones.

References

1. Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., CO₂ capture by a task-specific ionic liquid. *Journal Of The American Chemical Society* **2002**, 124, (6), 926-927.
2. Anderson, J. L.; Dixon, J. K.; Maginn, E. J.; Brennecke, J. F., Measurement of SO₂ solubility in ionic liquids. *Journal Of Physical Chemistry B* **2006**, 110, (31), 15059-15062.